

Appln. No. 09/787,348  
Amdt. dated February 11, 2004  
Reply to Office Action of November 14, 2003  
Docket No. 6009-4601

APPENDIX  
(Six (6) appended documents relating to metallurgical bonds)

## Thermal Spray Technology Glossary

| A | B | C | D | E | F | G | H | I | J | K | L | M | N | O | P | Q | R | S | T | U | V | W | X | Y | Z |

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### M

**\*Manifold.**

See Cylinder Manifold.

**\*Mask.**

A device for protecting a substrate surface from the effects of blasting or adherence of a spray deposit.

**Matrix.**

The major continuous substance of a thermal spraying coating as opposed to inclusions or particles of materials having dissimilar characteristics.

**\*Mechanical Bond.**

The adherence of a thermal spraying deposit to a roughened surface by the mechanism of particle interlocking.

**Melting Rate.**

The weight or length of spray wire or rod melted in a unit of time.

**\*Metallic Bond.**

The principal bond that holds metals together and is formed between base metals and filler metals in all processes.

This is a primary bond arising from the increased spatial extension of the valence electron wave functions when an aggregate of metal atoms is brought close together.

See also Bonding Force, and Ionic Bond.

**\*Metallizing.**

See preferred term Thermal Spraying.

**\*Metallurgical Bond.**

A nonstandard term for metallic bond.

**Molten Metal Flame Spraying.**

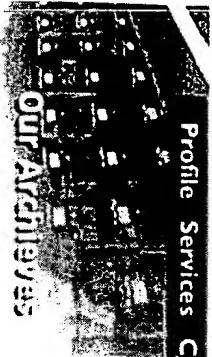
A thermal spraying process variation in which the metallic material to be sprayed is in the molten condition. See Flame Spraying (FLSP).

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Encl. 1



## Galvanizing

Paint as a mean to fight corrosion

Stainless Steels and Corrosion

What is the condition of your lifting devices?

New Methods to Inspect Aboveground Storage Tank

The inception of galvanizing brings us to the year 1712, when a French chemist named Melouin presented to the French Royal Academy a new protective coating by means of dipping a part in a melted zinc solution.

Today, lost associated with corrosion phenomena is estimated in billions of dollars. The zinc protective coating applied to metallic parts is known as galvanizing. The most common are hot dip galvanizing and electrochemical galvanizing. Other methods include Zinc spray metallizing, matoplasty (coating by zinc particles crushed with glass ball blasting), sherardizing (superficial diffusion of zinc into steel during heat treatment).

The hot dip galvanizing process remains the most widely used because of its low cost and its ease of adaptation to shape or other industrial processes. The following section will describe in detail this coating method.

### Hot Dip Galvanizing – The Process

The main goal of the hot dip galvanizing process is to coat a metallic part with a Zinc lair. That will act as a barrier to stop corrosion. This works because zinc oxidize slower than steel.

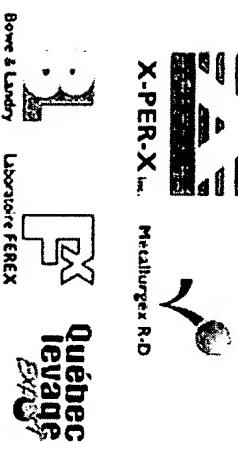
During this process, the part is directly dip in the melted Zinc solution. The immersion time, directly proportional to the part size, must be enough to allow the proper coating thickness. Usually, it is the time for the part to reach the melted bath temperature, around 450 °C. This time is between 3 and 10 minutes but can exceed 15 minutes for massive or geometrically complex parts. The thickness, the structure and the aspect of the coating will also vary based on the steel chemical analysis

Right now, the hot dip galvanizing process is applied to two sectors: the finished products and the semi-finished product such as tubes, wires, sheets, etc.

In order to galvanize parts, surface preparation according to specific steps is crucial before the dipping operation. Typically, three steps are necessary: degreasing, stripping and fluxing. These steps will directly affect the Zinc and steel reaction and, de facto, the coating in-service performance.

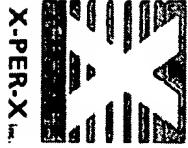
### How Does It Works?

When a part is dipped in and out of the zinc liquid bath, there is not only solidification of the zinc atop the steel substrate, but there is also a reaction call diffusion and the creation of a Iron-Zinc alloy (see photograph). The galvanizing is a metallurgical bond between the Zinc and the steel substrate, thus creating a metallic coating intrinsically part of the base material.



Bonne & Lurdy

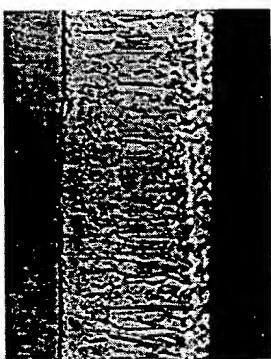
Laboratoire FEREX



Metallurgex R&D



Services



Characteristic structure of a galvanized coating

$\gamma$  Phase (Gamma): 21 to 28 % of Iron Content

The hardness of the different Iron-Zinc phases will contribute to the increase in impact and surface wear resistance. The hardness of the different phases varies from 60 Hv for the Eta lair up to 240 Hv for the Gamma lair. This characteristic is interesting and specific to the galvanizing process.

#### Corrosion Performance

A properly applied galvanizing coating can protect a part for 10 to 50 years depending on the environment (marine, industrial, rural, dry or a combination of two or more). The coating life is also directly related to its thickness.

Major advantages can easily be observed if you compare galvanizing to other coating methods such as paints and other metallic coating. The following table compares different coating systems between themselves.

#### Comparison between Hot Dip Galvanizing and Other Coating Systems

<b>Hot Dip Galvanizing</b>	<b>Other Metallic Coatings</b>	<b>Paints</b>
Long service life	Variable	Variable
Electrochemical protection of substrate	No electrochemical protection	No electrochemical protection of substrate
Whole part protected	Only accessible surfaces are protected	Only accessible surfaces are protected
Excellent impact resistance	Good impact resistance	Low impact resistance
Excellent wear resistance	Good wear resistance	Low wear resistance
Easy to inspect	Sometime difficult to inspect	Easy to inspect

Furthermore, scratches in the coating do not yield to corrosion of the steel. This is explained by the electrochemical difference between the zinc and the steel; the zinc will be corroded preferably to the steel, hence its protective property against steel corrosion. When exposed to an atmosphere affecting the expected life of the galvanizing, it is possible to paint the surfaces; this way a structure protected as such could theoretically last forever.

### When Things Go Wrong

Most problems with galvanizing origin from an inadequate surface preparation. As stated earlier, the surface preparation is crucial to obtain a quality coating. The following photographs show some coating failures related to an inadequate surface preparation.

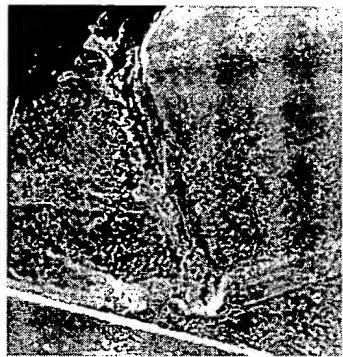


This photograph shows a surface defect related to an inadequate surface preparation. Paint residues, oil or grease stains left on a small area do not allow the liquid Zinc to properly bond with the steel during the hot dip galvanizing process.



This next photograph shows a recurring problem in galvanizing welded assembly. A flux deposit on a weld resulted in a poor adhesion of the Zinc during the galvanizing process. The flux deposits need to be removed by acid pickling prior to the galvanizing operation.

This last photograph shows a problem typically associated with assembly by welding, bolting, etc. After galvanizing, leftover acid from the pickling operation trapped between two surfaces reacts with the Zinc coating causing rust stains.



#### Prevention

As seen previously, hot dip galvanizing is an excellent choice to protect parts against corrosion. Our experience in monitoring coating processes will assure you of the best quality at every step, should it be surface preparations, chemical analysis of the solution bath, adherence tests or coating thickness verifications.

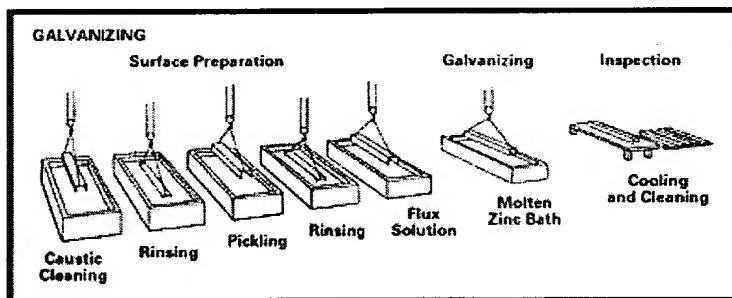


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## galvanizing process

- Surface Preparation
- Galvanizing
- Inspection
- The Metallurgical Bond
- Characteristics of Galvanized Surfaces
- Coating Thickness



### SURFACE PREPARATION

Surface preparation is the most important step in the application of any coating. In most instances, where a coating fails before the end of its expected service life, it is due to incorrect or inadequate surface preparation.

With galvanizing, the surface preparation process contains its own built-in means of quality assurance and quality control in that zinc will simply not react with a steel surface that is not perfectly clean. Any failures or inadequacies in surface preparation will be immediately apparent when the steel is withdrawn from the molten zinc and uncoated areas remain, and immediate corrective action is taken.

Conversely, a barrier coating applied by brush or spray to an inadequately prepared surface can pass initial inspection but fail on the job weeks, months or even years later, before the end of the expected service life of the coating.

Hot dip galvanizing is a factory-applied coating, and as such, primary responsibility for surface preparation as well as coating application falls with the galvanizer.

Surface preparation for galvanizing typically consists of three steps:

**Caustic Cleaning** — A hot alkali solution is often used to remove organic contaminants like dirt, paint markings, grease, and oil from the metal surface. Epoxies, vinyls, asphalt, or welding slag must be removed by grit blasting, sand blasting, or other mechanical means, before galvanizing. Removal of these materials is usually the responsibility of the fabricator.

**Pickling** — Scale and rust are normally removed from the steel surface by pickling in a dilute solution of hot sulfuric acid or ambient temperature hydrochloric acid.

Surface preparation can also be accomplished using abrasive cleaning as an alternative to or in conjunction with chemical cleaning. Abrasive cleaning is a process whereby sand, metallic shot, or grit is propelled

against the steel material by air blasts or rapidly rotating wheels.

**Fluxing** — Fluxing is the final surface preparation step in the galvanizing process. Fluxing removes oxides and prevents further oxides from forming on the surface of the metal prior to galvanizing and promotes bonding of the zinc to the steel or iron surface. The method for applying the flux depends upon whether the particular galvanizing plant uses the wet or dry galvanizing process.

In the dry galvanizing process, the steel or iron materials are dipped or "prefluxed" in an aqueous solution of zinc ammonium chloride. The material is then thoroughly dried prior to immersion in molten zinc. In the wet galvanizing process, a blanket of molten zinc ammonium chloride is used. This flux layer is floated on top of the molten zinc. The iron or steel that is being galvanized passes through the flux on the way into the molten zinc.

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## GALVANIZING

In this step, the material is completely immersed in a bath consisting of a minimum 98 percent pure molten zinc. The bath chemistry is specified by the American Society of Testing and Materials in Standard A 123. The bath temperature is maintained at approximately 850 degrees Fahrenheit.

Fabricated items are immersed in the bath long enough to reach bath temperature. The articles are slowly withdrawn from the galvanizing bath, and the excess zinc is removed by draining, vibrating, and/or centrifuging.

The chemical reactions that result in the formation and structure of the galvanized coating continue after the articles are withdrawn from the bath as long as these articles are near bath temperatures. The articles are cooled in either water or cold air immediately after withdrawal from the bath.

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## INSPECTION

The most important method of inspection for galvanized articles is visual. A variety of simple physical and laboratory tests may be performed for:

- Thickness
- Uniformity of the coating
- Adherence of the coating
- Appearance

Products are galvanized according to the long established, well accepted, and approved standards of the American Society for Testing and Materials (ASTM). Additional relevant standards are provided by the Canadian Standards Association (CSA) and the American Association of State Highway and Transportation Officials (AASHTO). ASTM standards cover everything from the minimum required coating thicknesses for various categories of galvanized items to the composition of the zinc metal used in the process.

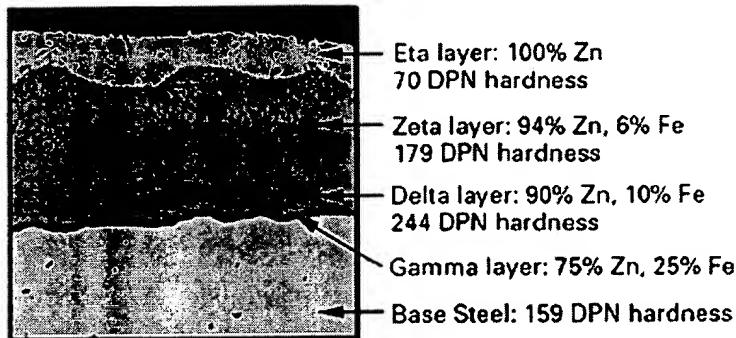
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## THE METALLURGICAL BOND

Galvanizing forms a metallurgical bond between the coating and underlying steel or iron. Galvanizing creates a barrier that is a part or extension of the metal itself. During galvanizing, the molten zinc reacts with the surface of the steel or iron

article undergoing galvanizing to form a series of zinc/iron alloys. A typical galvanized coating consists of three alloy layers and a layer of metallic zinc. Moving from the underlying metal surface outward, these are:

- The thin Gamma layer composed of an alloy that is 75 percent zinc and 25 percent iron
- The Delta layer composed of an alloy that is 90 percent zinc and 10 percent iron
- The Zeta layer composed of an alloy that is 94 percent zinc and 6 percent iron
- The outer Eta layer that is composed of zinc



Each layer is characterized by a measure of hardness called the Diamond Pyramid Number (DPN). The DPN is a progressive measure of hardness (i.e., the higher the number the greater the hardness). Typically, the Gamma, Zeta, and Delta layers are harder than the underlying steel. The hardness of these inner layers provides exceptional protection against coating damage through abrasion. The Eta layer of the galvanized coating is quite ductile, providing the galvanized coating with good resistance to damage by abrasion.

The galvanized coating is adherent to the underlying steel on the order of several thousand pounds per square (psi) inch. Other coatings typically offer adhesion rated at several hundred psi at best.

**These three factors, hardness, ductility, and adherence combine to provide the galvanized coating with unmatched protection against damage by rough handling during transportation to and/or at the job site as well as on the job.** The toughness of the galvanized coating is extremely important since barrier protection from corrosion is dependent upon the integrity of the coating. Other coatings damage easily during shipment or through rough handling on the job site. Experts will argue that all organic forms of barrier protection (such as paint) must be permeable to some degree. Correctly applied galvanized coatings are impermeable.

If the coating is physically damaged, the galvanizing will continue to provide cathodic protection to the exposed steel. If individual areas of underlying steel or iron of length and/or width of as much as 1/4" become exposed, the surrounding zinc will provide these areas with cathodic protection for as long as the coating lasts.

The galvanizing process naturally produces coatings that are at least as thick on the corners and edges as the coating on the rest of the article. As coating damage is most likely to occur at the edges, this is where added protection is needed most. Brush- or spray-applied coatings have a natural tendency to thin at the corners and edges.

**Because the galvanizing process involves total immersion of the material, it is a complete process; all surfaces are coated. Galvanizing provides both outside and inside protection for hollow structures. Conversely, hollow structures that are painted have no corrosion protection on the inside.**

**The inspection process for galvanized items is simple, fast and requires**

**minimal labor.** This is important because the inspection process required to assure the quality of many brush- and spray-applied coatings is highly labor intensive and uses expensive skilled labor.

**Galvanizing continues at the factory under any weather or humidity conditions.** Most brush- and spray-painted coatings are dependent upon proper weather and humidity conditions for correct application. The dependence of most brush- or spray-applied corrosion systems upon proper weather and humidity conditions often translate into costly construction delays at the job site.

The galvanizer's ability to work in any type of weather allows a higher degree of assurance of on-time delivery. Working under these circumstances, **galvanizing can be completed with short lead and turnaround times. A turnaround time of two or three days for galvanizing is common, and a week is standard.**

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#### CHARACTERISTICS OF GALVANIZED SURFACES

Three factors — hardness, ductility, and adherence — combine to give galvanized coatings unmatched resistance to damage by corrosion or rough handling.

- **Hardness.** Each layer of the galvanized surface is characterized by a measure of hardness called the Diamond Pyramid Number (DPN). The higher the DPN, the greater the hardness. Typically, the Gamma, Zeta, and Delta layers are harder than the underlying steel. This provides excellent resistance to damage from abrasion.
- **Ductility.** The Eta layer of the galvanized coating is quite ductile, or pliable, adding to the coating's abrasion resistance.
- **Adherence.** A galvanized coating is adherent to the underlying steel at several thousand pounds per square inch (psi). Other coatings typically offer adhesion rated at several hundred psi at best.

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#### COATING THICKNESS

ASTM specifications establish minimum standards for thickness of galvanized coatings on various categories of items. By the nature of the galvanizing process, the minimum standards specified by ASTM are routinely exceeded by galvanizers. Factors influencing the thickness and appearance of the galvanized coating include:

- Chemical composition of the steel
- Steel surface condition
- Cold working of steel prior to galvanizing
- Bath immersion time
- Bath withdrawal rate
- Steel cooling rate

The chemical composition of the steel being galvanized is very important. The amount of silicon and phosphorus present in the steel strongly influences the thickness and appearance of the galvanized coating. A silicon level of 0.04 percent or greater or a phosphorous level of 0.05 percent or greater in the steel will generally result in thick coatings consisting primarily of zinc-iron alloys. The carbon, sulfur, and manganese content of the steel also may have a minor effect on the galvanized coating thickness.

Certain steel compositions tend to accelerate the growth of zinc-iron layers. This may result in a finished galvanized coating consisting entirely of zinc-iron alloy. Instead of the shiny spangled appearance, the galvanized coating will have a dark gray, matte finish. This dark gray, matte galvanized coating will provide as much corrosion protection as a galvanized coating having the common spangled

appearance.

As the galvanizing reaction is a diffusion process, higher zinc bath temperatures and longer immersion times will generally produce somewhat heavier alloy layers. Like all diffusion processes, however, the reaction proceeds rapidly at first and then slows as layers grow and become thicker. Continued immersion beyond a certain time will have little incremental effect. In galvanizing of silicon bearing steels containing more than 0.04 percent silicon, the diffusion process significantly changes.

The thickness of the outer pure zinc layer is largely dependent upon the rate of withdrawal from the zinc bath. A rapid rate of withdrawal causes an article to carry out more zinc and generally results in a thicker coating.

ASTM and CSA specifications and inspection standards for galvanizing recognized that variations inherently occur in both coating thickness and compositions. Thickness specifications are stated in both average terms and as a minimum for any individual articles tested. Further, coating thickness measures must be taken at several points on each inspected article to comply with ASTM A 123.

Witt Industries is a member of the American Galvanizers Association and strictly adheres to these standards.

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## MetalForming Magazine

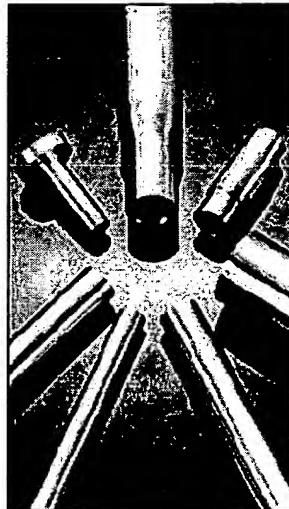
### Tech Update

#### Electropolished Stainless Offers Enhanced Corrosion Resistance

A service that improves the surface finish of large stainless steel vessels and tanks and increases the chrome-to-iron ratio is being provided by New England Electropolishing Co., Inc. of Fall River, MA. The process improves corrosion resistance for critical applications.

Electropolished stainless steel vessels and tanks feature uniform interior and exterior surface finishes down to RA 2, depending on part configuration. It also eliminates the need for hand finishing and passivating, while producing a smooth, high-luster finish.

New England Electropolishing Co. is equipped to handle objects up to 10 ft. long by 5 ft. wide and selectively can remove the high points on stainless steel vessels and tanks with 0.0001 in. precision. An electro-chemical process that is stress free, electropolishing removes surface impurities, deburrs and deeply passivates to resist the impregnation of bacteria.



#### Bi-Metallic Transition Joints

Custom-engineered bi-metallic transition joints now are available from Nuclear Metals, Inc. (NMI), Concord, MA. The joints feature a bond that is stronger than the weaker of its components. This type of joint often can be used in applications where clamps or fittings are impractical because of their size, weight and potential for failure.

NMI bi-metallic transition joints combine two dissimilar metals, such as titanium and stainless steel, to form a seamless metallurgical bond that is stronger than the weaker metal. Custom fabricated in sizes from 0.062 in. to 4 in. OD, these joints eliminate the use of mechanical fasteners that are subject to failure from vibration and pressure cycling.

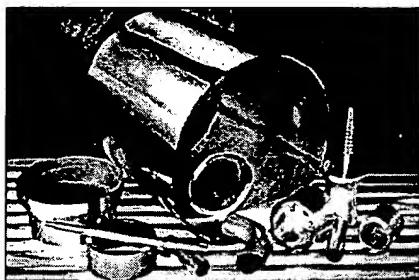
NMI bi-metallic transition joints are said to be ideal for applications where failure would be critical or there are space or weight restrictions. They are unaffected by severe thermal or pressure cycling. As an example of joint strength, a 304L stainless steel/6061-T6 Aluminum joint passes a burst test at 42,000 psi and has a tensile strength of 44,800 psi.

#### Post-Coating Process for Galvanized Steel

Researchers at Bethlehem Steel Corporation, Bethlehem, PA, have come up with a new post-coating process that improves both formability and weldability properties of zinc-coated sheet steel. The new treatment process, which has been awarded U.S. Patent 5,660,707, uses an alkaline solution to form a zinc oxide layer on the zinc or zinc alloy coating that is used to protect the surface of steel from corrosion.

Research has determined that the use of the alkaline solution on top of the zinc or zinc alloy coating imparts an ability to form the sheet steel into more complex parts and provides better weld acceptance by substantially reducing the number of weld tip changes needed in the welding process. In addition, because the alkaline treatment is applied after the steel leaves the plating or coating bath, these added properties are attained without introducing foreign substances into the coating bath.

The new patent recognizes C. Ramadeva Shastray, senior research engineer, Hot-Dip Coated Products, and Stavros G. Fountoulakis, supervisor, and Elmer J. Wendell, research analyst, Electrogalvanized & Tin Mill Products, at Bethlehem Steel's Homer Research Laboratories, as inventors of the process.



### Metal Tubing for R&D

Valley Metals, El Cajon, CA, announces a program to support R&D for product development by offering short run production of precision tubing on a timely basis. Valley Metals says it specializes in the manufacture of tubing from high-performance metal alloys.

### Laser Gauge Sorts to Print

General Inspection, Inc., Davisburg, MI, recently unveiled its new V-100 Laser Gauge. It is said to be the first high-speed quantitative, 100-percent inspection system that inspects and sorts entire parts to print. This allows corrective action to be taken to fix problems that are detected, although qualitative sorting doesn't tell precisely why a given part was rejected.

To operate the V-100, the user simply enters the part number, slides a part down the track and fills in the plus and minus tolerance for each dimension. When the part is to be inspected again, all that's required is to call up the part number and run.

The V-100 quantitatively gauges all profile dimensions within microns. Lengths, diameters, radii, tapers, complete thread geometry (pitch length and diameters, flank angles, root radii, truncation), etc. are measured to print at up to 300 parts per minute.



### Adjustable-Field Sensors



Banner Engineering Corp., Minneapolis, MN, has introduced adjustable-field photoelectric sensors that allow users to precisely detect objects within a defined sensing field, while completely ignoring reflective objects located beyond the sensing field cutoff point. These sensors provide increased flexibility by allowing the user to precisely and quickly define a unique cutoff point for each application.

The sensors feature electronic adjustment using a dual-element photodiode and hybrid geometry for more reliable performance in critical applications. Powered by 10v to 30v dc, sensors are available in a choice of two models with adjustable sensing cutoff points of either 2 in. to 6 in. (50 mm to 150 mm), or 5 in. to 16 in. (125 mm to 400 mm). Sensing field cutoff distance is adjusted easily using the 12-turn slotted brass potentiometer, which is clutched at both ends to prevent breakage.

The sensors are designed to withstand severe environmental conditions and impact. They also feature rugged input and output circuitry to prevent damage from high voltage transients and reverse polarity, along with providing high noise interference immunity. MF

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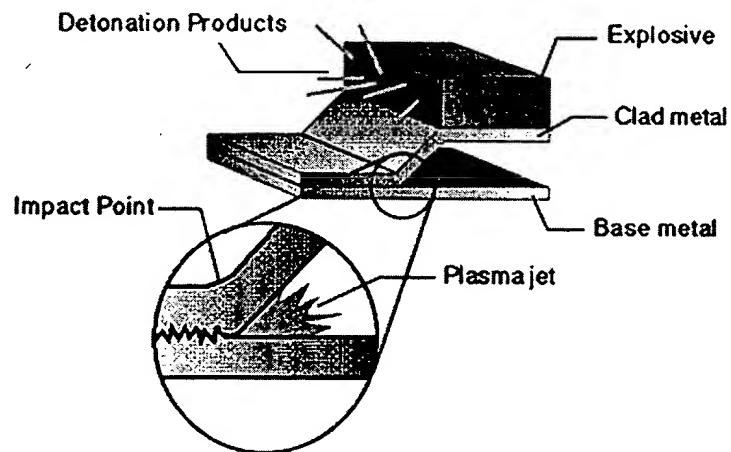
NEWS &amp; EVENTS

HUMAN RESOURCES

Technology Overview

## EWS™ Explosively Welded Stack

Explosive bonding is considered a solid state welding process that uses controlled explosive energy to force metals together at high pressures. The resultant composite system is joined with a high quality metallurgical bond. The duration involved in the explosive welding event is so short, that the reaction zone between the constituent metals is microscopic.



### How it works

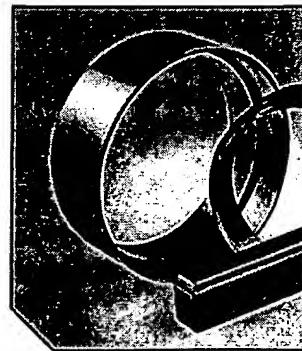
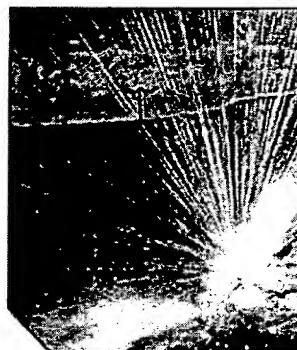
Plates are accelerated into one another with the forces generated by an explosive detonation. The "Flyer" plate yields to the force of the explosion as the detonation front moves across the surface of the plate. Forces at the collision point cause the first few molecular layers to liquify. Plasma jets between the surfaces, creating a full metallurgical weld, as the collision point accelerates across the plates. Explosive metal bonding is considered a cold joining process because the materials remain at or near ambient temperature and retain their original characteristics.

Weldable bi-metallic transition is one of the most common applications of explosively bonded metals. Forming - Explosively bonded metals routinely withstand subsequent forming operations. Forging - Explosively bonded metals are capable of withstanding the rigors of forging operations.

### Custom Products

Pacific Aerospace & Electronics, Inc. is committed to supporting our customers in the integration of explosively bonded metals into their product lines. Our friendly engineering staff not only possesses the specific expertise and knowledge of explosive metalworking, but is also comprised of experienced mechanical engineers, metallurgists, chemists, and physicists capable of analyzing every aspect of your custom application. We are experienced in full product/application development. Contact a representative from our engineering staff to discuss your needs.

› [Technical Information](#)



- [Standard Clad Metal Products \[pdf document\]](#)
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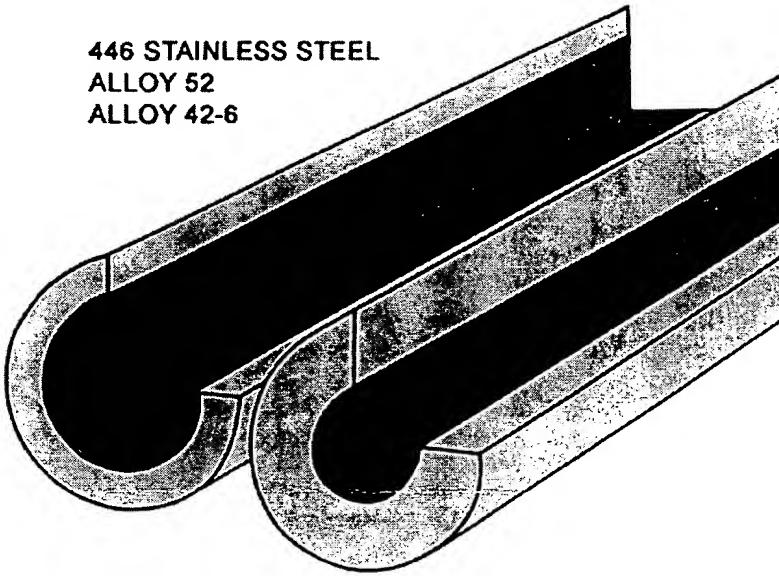
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ALLOY 52  
ALLOY 42-6****Anomet's Copper Cored/Clad Glass Sealing alloys feature:**

- Complete Metallurgical Bond – This means complete hermetic sealing between the metals, excellent mechanical strength, ductility and greater reliability
- Copper Core – Permits simple electrical connections and greater conductivity which means a smaller conductor than solid for the same power requirements.
- Cored vs. Clad – Unique property ratio of 446SS, Alloy 52, copper can be made (i.e. dial sealing alloy to diameter of conductor)
- Custom Processing & Other / Surface Finish, and packaging customized to your specific requirements.

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